

PREPARATION AND CHARACTERIZATION OF BIOSORBENTS PREPARED FROM SEEDS OF *POLYALTHIA LONGIFOLIA*

Kavita S. Mundhe^{1*}, Anjali D. Ruikar², Nirmala R. Deshpande³ and Rajashree V. Kashalkar³

¹Anantrao Thopte College, Bhor. Dist. Pune, Maharashtra, India.

²Fergusson College, Pune, Maharashtra, India.

³Dr.T.R.Ingle Research Laboratory, Department of Chemistry, S.P.College, Tilak Road, Pune- 411030, India.

Received on: 20/04/2020

Revised on: 10/05/2020

Accepted on: 31/05/2020

*Corresponding Author

Kavita S. Mundhe

Anantrao Thopte College,
Bhor. Dist. Pune,
Maharashtra, India.

ABSTRACT

In order to prepare low cost carbons with desired properties various industrial and agro waste materials have been used as precursors. The adsorption of pollutants from an aqueous solution is frequently used to test the adsorption capability of various adsorbents. By changing the preparation and activation conditions, surface structure and pore size distribution can be modified. Physical and chemical activation involves treatment of precursor to produce carbon of desired properties. Chemical treatment modifies the surface structure and increases the adsorption capacity. Adsorbents have been prepared from seeds of *Polyalthia longifolia* by various treatments. Adsorption on biosorbents is due to the various functional groups present on the surface. These generally consist of carbonyl, amine, hydroxyl groups which can be analyzed qualitatively using FTIR and SEM techniques and quantitatively by Bohem's titration. The proximate analysis gives information regarding properties such as ash content, pH and bulk density. The effect of lignocellulosic structures on their carbons is also observed. Use of such newer materials will result in carbons having diverse structures and thereby adsorption capacities. The peaks in the FT-IR of adsorbents, strongly supports the presence of surface groups obtained by Boehm's titration. It is observed that there are significant changes in the band intensities of these adsorbents. Association of peak at 1371 cm^{-1} and many weak peaks had disappeared in SATM, indicating that the weak bonds disappeared under chemical treatment.

KEYWORDS: Biosorbents, *Polyalthia longifolia* seeds, Characterization, Bohem's titration.

INTRODUCTION

Carbon materials are unique and having variety of applications in the field of industry such as oil and natural gas, food, pharmaceuticals, water treatment, gold recovery, production of fine and bulk chemicals and catalysis. Activated carbons due to high specific area and porosity are effective in removing pollutants. The advantages of activated carbon as adsorbents in effluent treatment gives good quality effluent and design and operation of the process is simple.^[1] In addition to purification of gases and liquids, carbon materials are used as catalyst and catalyst support. High cost and large demand of activated carbon necessitates the need for the exploration of new sources of carbon materials with desired physicochemical properties. The carbon precursor and the method of preparation are the determining factors of the textural and surface properties of carbon materials.^[2]

Literature survey reveals that activated charcoal has been prepared from bagasse, coconut shell, coffee beans, cotton seed hulls, wood saw dust, walnut shell grapes seeds, eucalyptus, olive and peach stone have been found

to be suitable precursors producing high carbon and low ash contents.^[3] The materials like tree barks, cotton capsule shells, saw dust, rice straw, ground nut husk carbon and tea leaves have been investigated for the removal of pollutants from waste water in the last few decades. In some cases the raw materials were used as an adsorbent with or without thermal/chemical treatment. Literature survey also reports that the agro waste materials without any treatment can be effectively used for the removal of pollutants from waste water viz. maize bran for removal of chromium (II) ions. Literature reports revealed that various researchers investigated the potential of biosorbents in removing pollutants from waste water.^[4] *Polyalthia longifolia* is a garden tree generating large amount of seeds. These are not useful as animal feed stock and thus become a potential source of garden waste. It was therefore thought worthwhile to investigate the potentials of these seeds – treated and untreated- for various applications. Adsorbents have been prepared from these seeds by various treatments.

MATERIALS AND METHODS

Preparation of adsorbents

Untreated Material (PM)

The seeds of *P. longifolia* were collected from the nearby garden in Pune Maharashtra, India during the month of July and August. The seeds were washed to remove dirt and earthy materials and air dried. The dried seeds were crushed, powdered and sieved to particle size 0.063 mm and stored in air tight bottle for further use as an adsorbent, labeled as Powdered Material, 'PM'.

Carbonized Material (CM)

The carbonization of dried seeds was done in absence of air in an air tight bottle, till the constant weight is obtained. The seeds were then ground and sieved to obtained uniform particle size of 0.063 mm. The carbonized material was stored in an air tight bottle and named as Carbonized Material, 'CM'.

Sulphuric Acid Treated Material (SATM)

Dried and crushed seeds of *P. longifolia* (PL) were taken in a beaker and mixed with concentrated sulphuric acid in a ratio of 2:1 with vigorous stirring (Acid volume: weight of crushed *P. longifolia* seeds).^[5,6] Charring of seeds occurred immediately accompanied by evolution of fumes. When the reaction subsided, the mixture was left over at room temperature for a period of 24 hours, to facilitate charring of the material. At the end of this period, the product was washed with large volumes of water to remove free sulphuric acid and dried at 100 °C. The dried product was then ground and sieved to obtained uniform particle size of 0.063 mm. This material was then kept in an air tight bottle for further use as an adsorbent and referred as sulphuric acid treated material 'SATM'.

EDTA treated material (EDM)

The chemically activated material was EDTA- modified by reported method.^[7] 17 gm of SATM was refluxed in a mixture of 300 ml pyridine and 56.7 gm EDTA for 3 hours at 70 °C. The mixture was cooled, filtered and washed with distilled water. The washed EDTA-modified material was then dried at 50 °C for 12 hours. This was then stored in air tight bottle, used as the modified adsorbent for the analysis and labeled as 'EDM'.

Characterization of adsorbent

The proximate analysis of the resulting adsorbents PM, CM, SATM & EDM was carried out according to the standard procedure.^[8] and then quantitatively analyzed for surface functional groups by using Boehm titration. FT-IR and SEM techniques are used for characterization of surface morphology. Results are given in Table 1.

Boehm titration

Boehm titration is one of the most widely used method to quantify and differentiate surface groups on activated carbon. The amount of acidic groups on the activated carbon is calculated under the assumption that 0.05N

sodium bicarbonate neutralizes strong acid groups, 0.05N sodium carbonate neutralizes both carboxylic and lactone groups, 0.05N sodium hydroxide neutralizes carboxylic, lactone and phenolic groups and 0.1N sodium ethoxide neutralizes carbonyl groups. Our method is similar to that used by.^[9,10] Adsorbent (0.500 gm) was mixed with 50 ml 0.05 N sodium hydroxide, sodium carbonate, sodium bicarbonate, and sodium ethoxide solutions respectively. Corresponding solutions of 50 ml volume without solid samples were used as blanks. The flasks were covered with aluminium foil and were shaken for 24 hr at 150 rpm. 10 ml of supernatant from each flask was then titrated with 0.05 N hydrochloric acid. The difference in blank and back was used to calculate milimoles of corresponding groups.

Fourier-Transform Infra - red (FT-IR) analysis

FT-IR analysis was performed in order to characterize the functional groups of the adsorbent. A Perkin -Elmer spectrum RX/FT-IR system was used for spectral analysis. Infra red spectra of prepared adsorbents are shown in Fig. 1- 4.

Scanning Electron Microscope (SEM) analysis

The morphology of prepared adsorbents was studied using scanning electron micrograph for analyzing micro and macropores present on the surface of adsorbents. The scanning electron micrograph of adsorbents (0.063mm size) was obtained using Scanning Electron Microscope (Model Leica-Stereoscan-440). SEM of the prepared adsorbents are depicted (Fig.5- 8).

RESULTS AND DISCUSSION

PM, CM, SATM and EDM have been characterized in terms of pH, bulk density, moisture content, ash content and surface functional groups. Results obtained are shown (Table 1). The bulk density of PM and SATM have been found to be 0.5092 g/ml and 0.5212 g/ml. High value of SATM indicates good carbonization of seeds. Low ash content of the adsorbent is considered to be superior and better quality of the adsorbent. The ash content of PM, CM, SATM and EDM are found to be between 2.20% - 3.54% indicates that, they are good adsorbents. The presence of surface functional groups plays an important role in the adsorption capacity and the removal mechanism of the adsorbates.^[11] The surface chemistry of carbon is determined to a large extent by the number and the nature of the surface functional groups. The presence of these groups results in an acid/base character of the carbon surface. Carbon-oxygen surface compounds play an important role in influencing surface reactions, surface behavior, hydrophilicity, electrical and catalytic properties of carbons. Cationic or anionic exchange capacities have been observed for carbons depending on surface functionality.^[12] The existence of different types of functional groups has been identified by means of FT-IR and Bohems titrations. Boehm titration method helps to determine the number of the oxygenated surface groups. The presence of surface oxygen containing functional groups like

carboxylic, lactonic and phenolic groups constitute the acidity of the material while oxygen free Lewis basic sites constitute the basicity.

The FT-IR spectrum of PM, Figure 1 shows a broad peak between 3550-3150 cm^{-1} , indicating the presence of polyhydroxylated compound. The peak at 2937 cm^{-1} demonstrates the presence of saturated alkane C-H stretching. The peak at 1735 cm^{-1} indicates the presence of carbonyl. The strong band at 1639 cm^{-1} depicts the presence of C=C bond. Association of peak at 1371 cm^{-1} displays presence of $-\text{CH}_3$ group. The peaks at 1246, 1154 and a strong peak at 1018 cm^{-1} indicate the presence of $-\text{O}-\text{C}=\text{O}$ acyl oxygen and etherial linkages of ester in addition to the carbonyl and the carboxylate groups present on the material.

The IR spectrum of CM, Figure 2 shows a peak at 3643 cm^{-1} which indicates the presence of free $-\text{OH}$ groups and a broad peak at 3417 cm^{-1} indicates associated $-\text{OH}$ groups. The presence of weak peak at 3057 cm^{-1} is due to aromatic C-H stretching. A peak at 2881 cm^{-1} manifests C-H stretching of saturated alkane. The peak at 1766 cm^{-1} explains the presence of carbonyl group of cyclic ester. The peaks at 1591 and 1497 cm^{-1} confirms the presence of aromatic ring. The presence of peaks at 1380, 1128 and 1080 cm^{-1} point to the presence of $-\text{O}-\text{C}=\text{O}$ acyl oxygen and etherial linkages of ester function in addition to the carbonyl and the carboxylate groups present on the material.

The FT-IR spectrum of SATM, Figure 3 shows very small peak at 3433 cm^{-1} is of associated $-\text{OH}$ bonded polyhydroxyl groups. Here no broad band is observed as in PM may be due to intermolecular hydrogen bonding (commonly appearing between 3550 and 3200 cm^{-1}). The peaks at 2881 and 2814 cm^{-1} makes an appearance for C-H stretching of saturated alkanes. The peak at 1703 cm^{-1} is due to conjugated C=O group. Stretching frequency absorption illustrated at 1602 and 1487 cm^{-1} proves the presence of aromatic ring. The peaks at 1217, 1080 and 1036 cm^{-1} is due presence of $-\text{O}-\text{C}=\text{O}$ acyl oxygen and etherial linkages of ester function which are present in addition to carbonyl and carboxylic groups.

IR of EDM, Figure 4 shows a broad peak at 3433 cm^{-1} assignable to $-\text{OH}$ group. The peak at 2883 cm^{-1} is due to C-H stretching of saturated alkanes. The peak at 1712 cm^{-1} is C=O group. The peaks at 1602 cm^{-1} and 1502 cm^{-1} presence of aromatic ring. The acyl oxygen and etherial linkages of ester function was confirmed by the presence of peaks at 1215 cm^{-1} and 1037 cm^{-1} .

Quantitative estimation of surface functional groups by Boehm's titration showed that the carbonyl groups are present in high concentration followed by lactone, phenolic and carboxylic groups. pH values of all adsorbents were consistent with the results of Boehm titration which indicates that more amount of carbonyl

functional groups are present on the surface of the adsorbents resulting in the basicity of the carbon surface. It was found that there are significant differences in the quantity of surface functional groups found in these adsorbents (Table 1). Acid treatment can keep nearly the same pore structure but change the surface chemistry significantly. Surface chemistry is apparently the key to the change of adsorption capacity. From results of Bohems titration it is quite clear that the amounts of functional groups in the adsorbents are significantly different and also vary from one adsorbent to another. From these observations it can be concluded that these four adsorbents prepared from *P. longifolia* seeds contain various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic, carboxylic and lactone groups which might provide sufficient binding sites for adsorption of cationic dye like methylene blue and heavy metals through different mechanisms. Changing methods and conditions of production process would improve the chemical characteristics of the adsorbent.

Scanning Electron Micrographs of adsorbents are as shown in (Figure 5 to 8). SEM analysis showed that cavities are already present on the surface. This may be due to production of Carbon of different porosity from lignocellulosic material present in the seeds of *P. longifolia*.^[13] Scanning Electron Micrographs of these adsorbents shows different structural features with non-uniform size and surface indicates the porous structure of adsorbents. SEM of PM clearly shows the heterogeneous surface structure which is not observed in other adsorbents. Chemical activation appears to develop more uniformity in the surface structure.

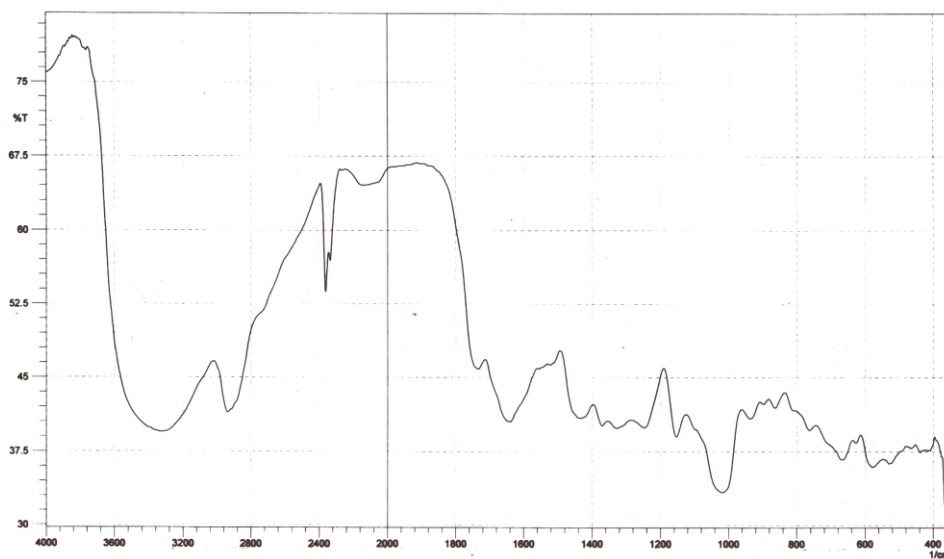


Figure 1: FTIR spectrum of PM.

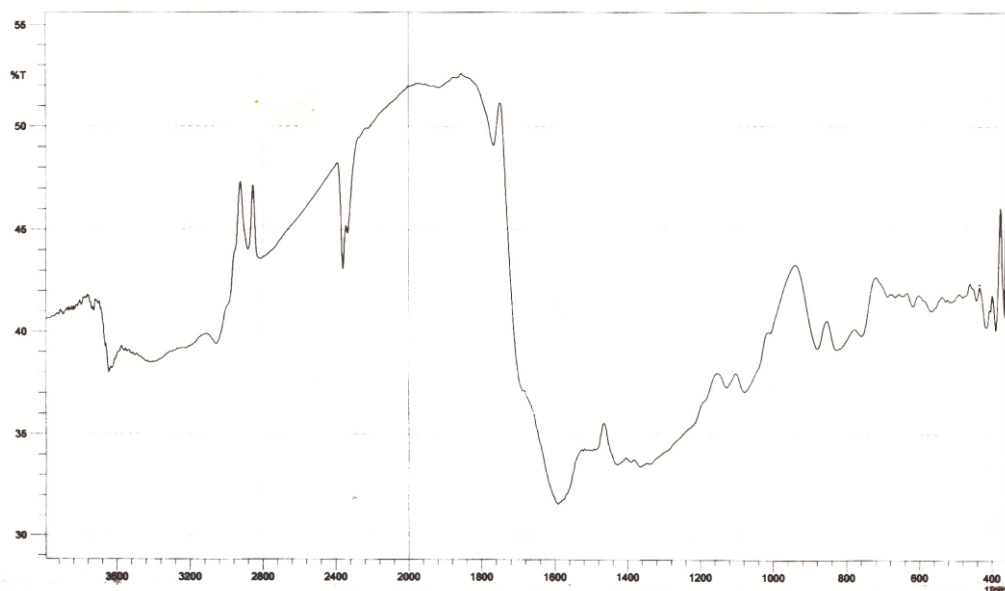


Figure 2: FT - IR spectrum of CM.

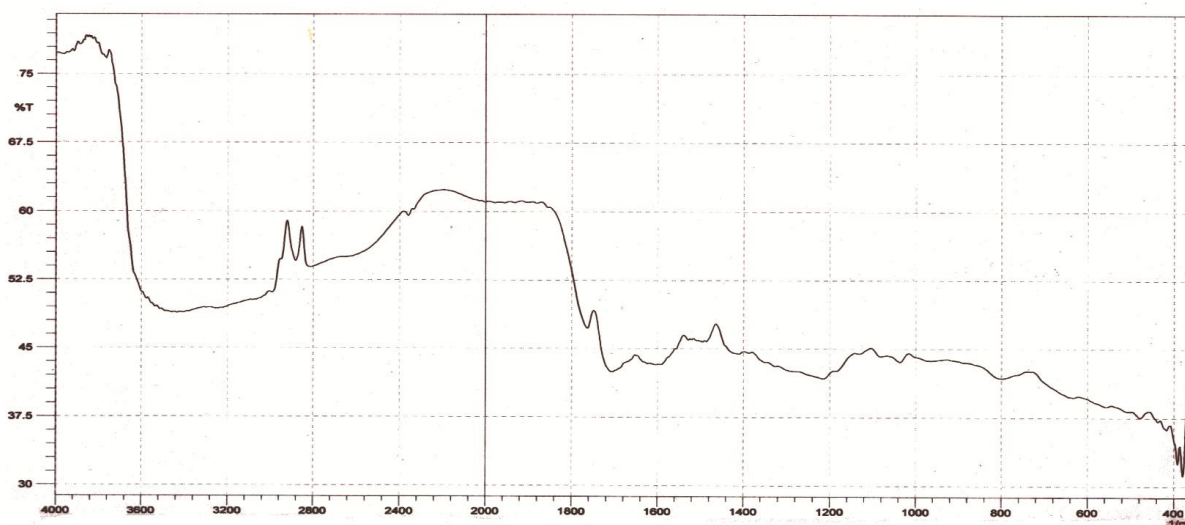


Figure 3: FT - IR spectrum of SATM.

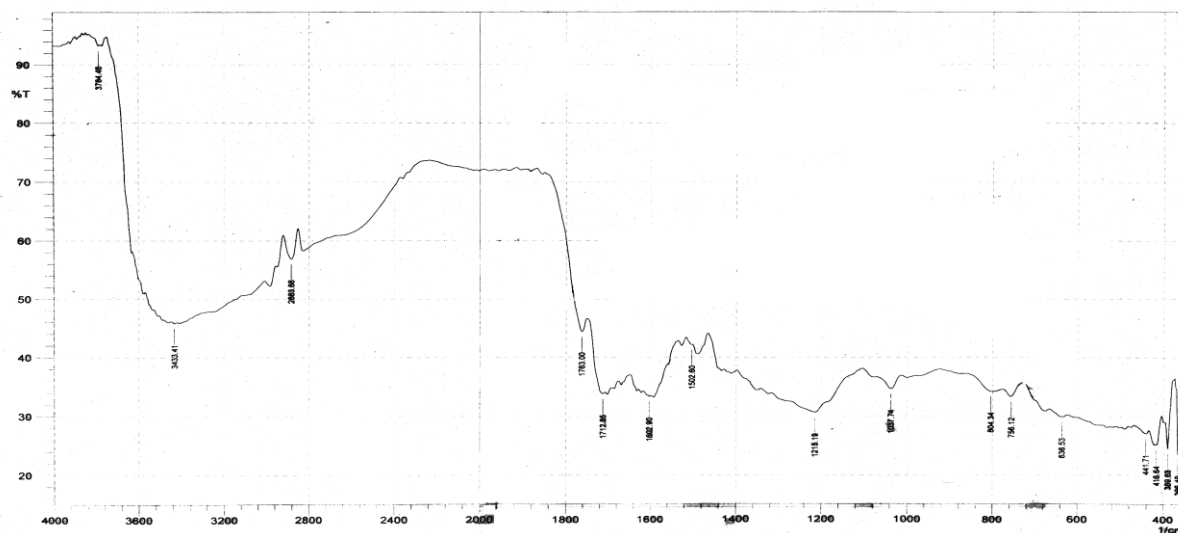


Figure 4: FTIR Spectrum of EDTA.

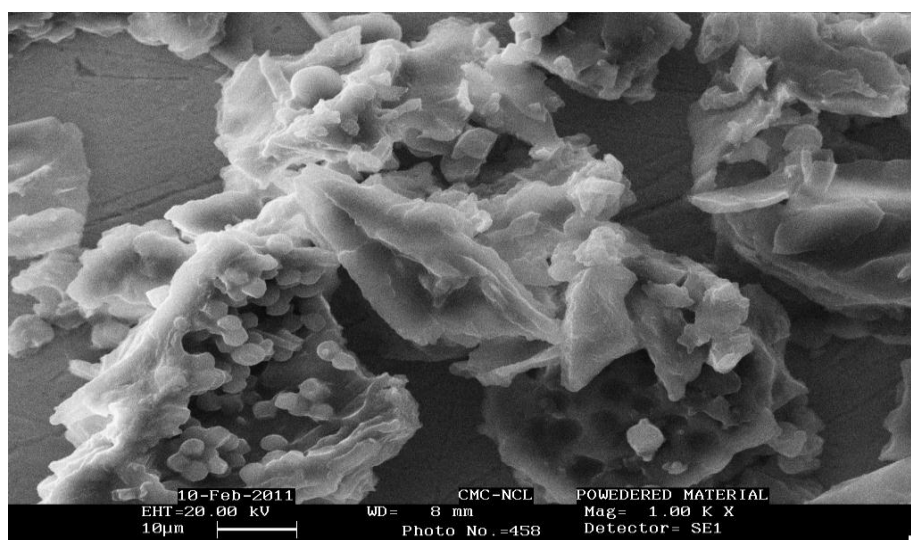


Figure 5: SEM of PM.

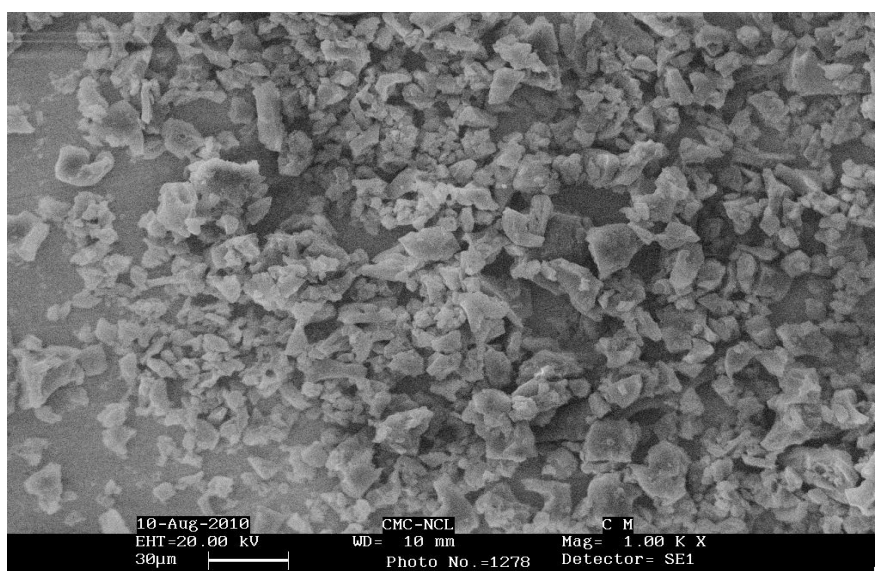


Figure 6: SEM of CM.

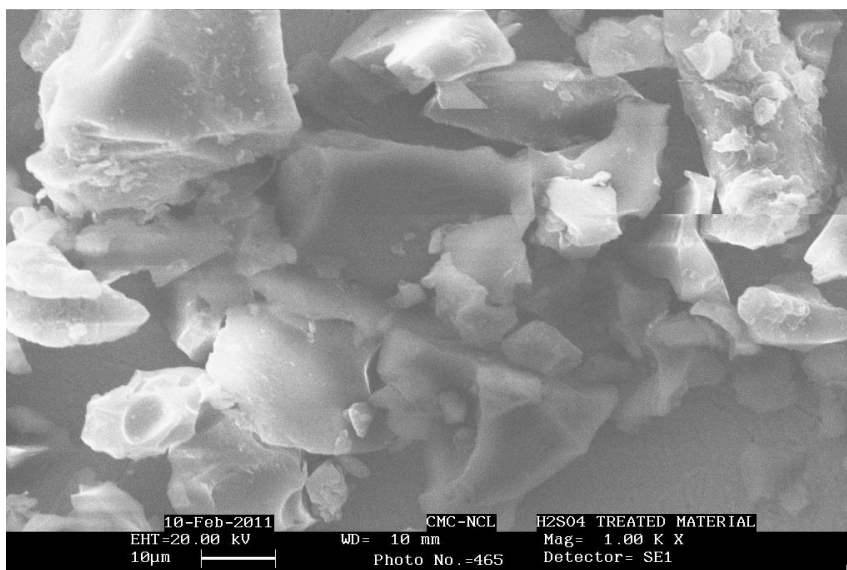


Figure 7: SEM of SATM.

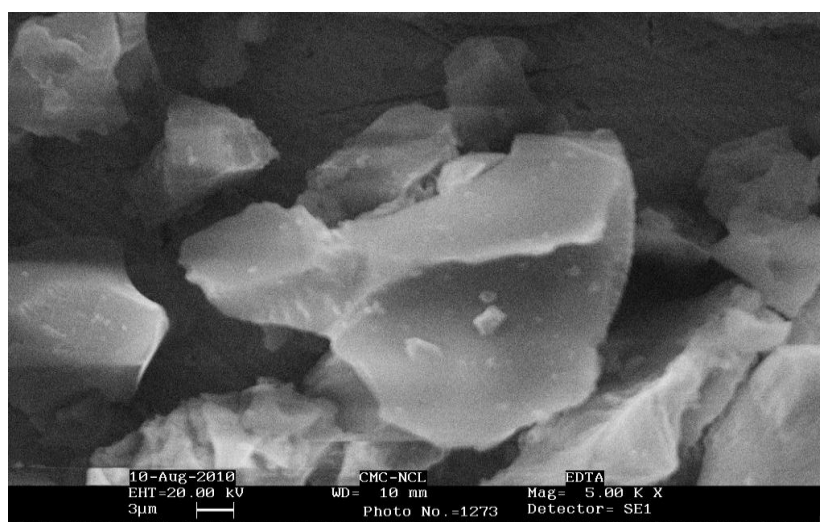


Figure 8: SEM of EDM.

Table 1: Characterization of Biosorbents prepared from *P. longifolia* seeds.

Physical Parameter	Value (PM)	Value (CM)	Value (SATM)	Value (EDM)
P H	5.76	5.98	6.5	6.0
Bulk density(gm/ml)	0.5092	0.5082	0.5212	0.5120
Moisture (%)	8.23	7.34	10.62	8.53
Ash content (%)	3.54	3.21	2.58	2.20
Surface acid groups (meq/g)				
carbonyl group	0.4875	0.3375	0.7875	0.525
lactone group	0.1213	0.0481	0.2996	0.0908
phenolic group	0.0049	-	0.0286	0.0378
carboxylic group	0.00065	0.00065	0.0052	0.00065

CONCLUSION

All the adsorbents exhibit low ash content. Quantitative analysis by Bohems titration support the information obtained from FT-IR regarding surface functional groups of the adsorbents.

Data obtained from Bohems titrations indicate that the functional groups are present in the adsorbents in the following order SATM, EDM, PM, CM. It also revealed that a given adsorbent contains maximum amount of carbonyl groups and minimum amounts of carboxylic groups. From SEM analysis it can be concluded that although a slight porous structure is observed in PM, the

surface is quite heterogeneous. Chemical treatment appears to make the surface homogeneous.

ACKNOWLEDGEMENT

Authors are thankful to the Head, Department of Chemistry, S. P. College, and the Principal S. P. College, Pune, Maharashtra, India for providing the necessary laboratory facilities for the work. The authors are also thankful to the principal, Anantrao Thopte College Bhor, Dist. Pune, Maharashtra, India for their constant support to carry out this work.

REFERENCES

1. Xiaoge Chen, S. Jeyaseelan, N. Graham, *Waste Management*, 2002; 22: 755.
2. M. Olivares- Marin, C. M. Gonzalez-Gonzalez, A. Macias- Garcia, V. Gomez- Serrano, *Applied Surface Science*, 2006; 252: 5967.
3. M. A. O. BADMUS, T. O. K. AUDU and B. U. ANYATA. *Turkish J. Eng. Env. Sci.*, 2007; 31: 251 – 263.
4. Gardea-Torresday et al., *J. Hazardous Material, B*, 2002; 91: 95- 112.
5. Huy Deng et al., 2011 & Ahmet Ornek et al., 2007.
6. Dr.C.K.Kokate. *Practical Pharmacognosy*, Fourth Edition, G Print Process, Delhi, 2008; 107-111.
7. J. C. Igwe, O. C. Okpareke, A. A. Abia. *Intern. J. Chem.*, 2005; 15(3): 187-191.
8. Susmita Dutta et al., *Desalination*, 2011; 275: 26 – 36.
9. Krisztina LASZLO et al., *Analytical Sciences*, 2001; 17: i1741 – i1744.
10. V. Strelko Jr. et al., *Carbon*, 2002; 40: 95 – 104.
11. M.M. El-Halwany. *Desalination*, 2010; 250: 208 – 213
12. Boehm H P. *Carbon*, 1994; 32(5): 759-769.
13. D.Kavitha et al. *Bioresource Technology*, 2007; 98(1): 14 -21.